# SCIENCE FOR CERAMIC PRODUCTION

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## FORMATION OF A POROUS STRUCTURE IN A GRANULATED GLASS CERAMIC MATERIAL FROM ZEOLITE-BEARING ROCK WITH ALKALI ADDITIVES

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The possibility of producing foam glass ceramics from zeolite-bearing rocks is investigated. It is established that milling the zeolite-bearing material to a particle size below 0.50 mm and adding 13.8% alkali ensures at the firing temperature of 850°C the production of a material of bulk density 340 kg/m$^3$, strength 1.6 MPa, and water absorption 13%. The granulated foam zeolite with the alkali additive is a glass ceramic material of higher strength than foam glass.

An important path for saving power resources is the use of efficient heat-insulating construction materials. Data on heat-insulating materials produced in most industrialized states in Europe and North America (Sweden, Germany, USA, and other countries with milder climates than Russia) report production of 5 – 7 times more per capita than Russia. The leading position in the production of thermal insulators is taken by mineral wool (75%), next in the descending order follow polymer-based materials (foam polyurethane, foam plastics etc.) — 20% and products based on lightweight (mainly cellular) concrete — 3%. Other kinds of thermal insulators take 2% of the total production volume. In particular, foam glass is one of the most efficient and durable heat-insulating materials. Foam glass is a cellular material produced by foaming finely milled glass powder using a pore-forming agent. The initial material, as a rule, is glass waste; the problem of collecting and pretreatment of cullet is a significant one.

The present study considers the possibility of producing a foam glass-ceramic material from zeolite-bearing rocks, which would be the analogue of foam glass. Zeolites are skeletal aluminosilicates whose structure includes communicating cavities occupied by cations of different elements (more frequently, alkali and alkaline-earth) and water molecules that can be easily removed or absorbed by the structure, which generates ionic exchange and reverse dehydration without destroying the structure [1].

The studies carried out in Russia and abroad showed the promise of obtaining high-quality granulated and block heat-insulating structural foam materials at a temperature of 1150 – 1200°C, from zeolite-bearing rocks, including rocks with medium and low zeolite mineralization (10 – 50%) [2 – 5].

The purpose of our study is to consider the possibility of obtaining a lightweight glass ceramic granulated material based on zeolite-bearing rock from the Sakhaptinskoe deposit (Krasnoyarsk Region) with a foaming temperature of 800 – 900°C, as well as study the effect of milling fineness of this rock on the properties of the materials.

The mineral composition of the zeolite-bearing rock from the Sakhaptinskoe deposit includes zeolite (clinoptillolite), quartz, feldspar, and argillaceous minerals (montmorillonite). The chemical composition of this zeolite-bearing rock is close to glass compositions; we observe only a deficit of alkali oxides (wt.%): 66.10 $SiO_2$, 0.34 $TiO_2$, 12.51 $Al_2O_3$, 2.36 $Fe_2O_3$, 2.27 CaO, 1.66 MgO, 1.04 $Na_2O$, 3.24 $K_2O$, and 10.28 calcination loss.

Differential thermal analysis (Fig. 1) of the zeolite-bearing rock indicates that zeolite under heating gradually releases water without disintegration of the aluminosilicate skeleton. The endothermic effect at 92°C with 7.7% weight loss is related to the release of free water, and the endothermic effect at 180°C is related to the release of interpacking water from montmorillonite and zeolite water from clinoptillolite. The removal of zeolite water ends at a temperature of 400°C. The further weight loss is due to the release of water bonded to cations $Na^+$ and $K^+$ from zeolite and the constitution water from the montmorillonite structure: these are the endothermic effects at 500 and 620°C. The endothermic ef-

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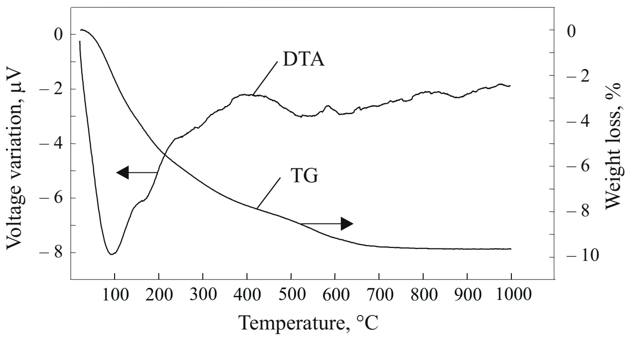


**Fig. 1.** DTA and TG diagrams of zeolite-bearing rock.

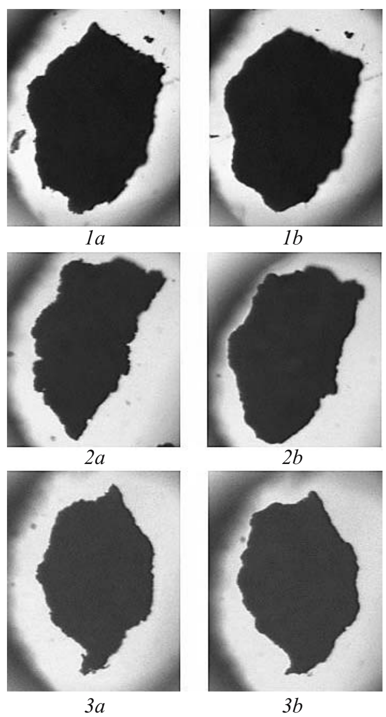


**Fig. 2.** Photos of foam zeolite samples of materials with milling fineness < 0.25 mm (*1*), < 50 mm (*2*), and < 1.00 mm (*3*) at temperatures of 24°C (*a*) and 850°C (*b*), respectively.

fect in the temperature interval of 850 – 900°C (the maximum at 860°C) does not involve a weight loss and corresponds to the formation of low-melting binary ($Na_2O - SiO_2$) and ternary ($Na_2O - Al_2O_3 - SiO_2$, $Na_2O - CaO - SiO_2$) eutectic melts.

**TABLE 1**

| Sample of granulated foam zeolite | Size of zeolite-bearing rock particles, mm | Properties of granules | | | Bulk density of foam zeolite, kg/m$^3$ |
|---|---|---|---|---|---|
| | | strength, MPa | mean density, kg/m$^3$ | water absorption, % | |
| 1 | < 0.25 | 1.56 | 560 | 14 | 320 |
| 2 | < 0.5 | 1.60 | 560 | 13 | 340 |
| 3 | < 1 | 1.60 | 570 | 10 | 350 |

To study the effect of milling fineness of the zeolite-bearing rock on the properties of the granulated foam zeolite, the material was milled to a particle size < 0.25, < 0.50, and < 1.00 mm. The granules were molded on a plate granulator to which an alkali component was fed. Molded granules were dried and then heat-treated at 850°C.

Differential thermal analysis of mixtures prepared from material with different milling fineness shows that the first endothermic effect corresponds to the removal of hydrate water, interpacking montmorillonite water, and zeolite water; the weight losses of samples with particle sizes < 0.25, < 0.50, and < 1.00 mm were equal to 10.97, 12.01, and 11.55%, respectively. The second endothermic effect at the temperature of 530 – 580°C is related to the removal of crystallization water and the decomposition of montmorillonite; the weight losses of the samples with particle size < 0.25, < 0.50, and < 1.00 mm were equal to 3.20, 2.31, and 3.79 %, respectively.

The formation of an eutectic melt with water removal as a consequence of NaOH reacting with silica occurs at 670 – 920°C. The weight losses of samples with particle size < 0.25, < 0.50, and < 1.00 mm amount to 0.33, 0.68, and 0.36%, respectively.

The release of water in the first and the second thermal effects does not lead to foaming. The combination of the melt formation and water release (the third thermal effect) provides for the formation of a porous structure.

Analysis of the thermograms of the zeolite-bearing rock indicates that adding an alkali solution ensures the introduction of hydration water in the form of sodium hydroxide, which is released in the formation of sodium silicate according to the exchange reaction:

$$2NaOH + SiO_2 \xrightarrow{700-830°C} Na_2SiO_2 + H_2O.$$

Sodium silicate at the same time participates in the formation of the melt.

Furthermore, to study the behavior of the material under heating, we employed a TMS 93 high-temperature microscope (Germany), which made it possible to visually observe the transformation of the material under firing and determine the foaming temperature. It has been established that the foaming start temperature for foam-zeolite materials is 850°C. The maximum volume increase was observed in samples with milling fineness < 0.50 mm (Fig. 2).

The granulated foam zeolite was tested according to standard GOST 9758–86 (Table 1).

The results of the microscopic study of the granulated foam zeolite are shown in Fig. 3, whereas Fig. 4 shows the phase composition of a foam-zeolite sample identified by x-ray phase analysis. It can be seen in Fig. 4 that the content of the amorphous phase in fired samples is 38.6% and the crystal phase is represented by feldspar (sanidine and albite), quartz, diopside, and spinel.

Thus, milling zeolite-bearing materials to a particle size below 0.50 mm and adding 13.8% alkali produces at the fir-

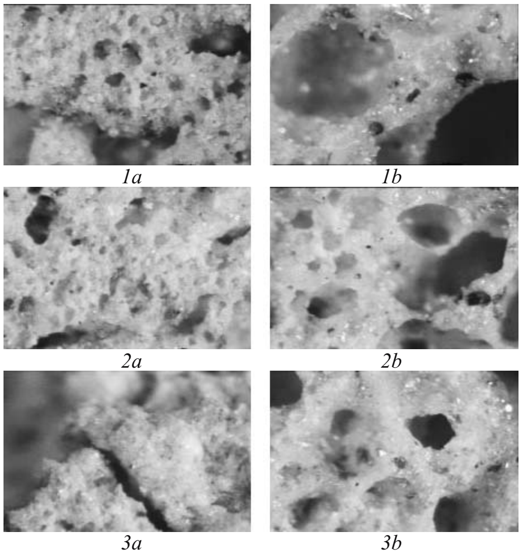


**Fig. 3.** Microscopic photos of foam zeolite granules (× 50) from materials with milling fineness < 0.25 mm (*1*), < 50 mm (*2*), and < 1.00 mm (*3*): *a* and *b*) central and peripheral parts of the granules, respectively.

ing temperature of 850°C a material with bulk density 340 $kg/m^3$, strength 1.6 MPa, and water absorption 13%. As for its phase composition, the granulated foam zeolite with the alkali additive is a glass ceramic material with 38.6% amorphous phase content and is stronger than foam glass.

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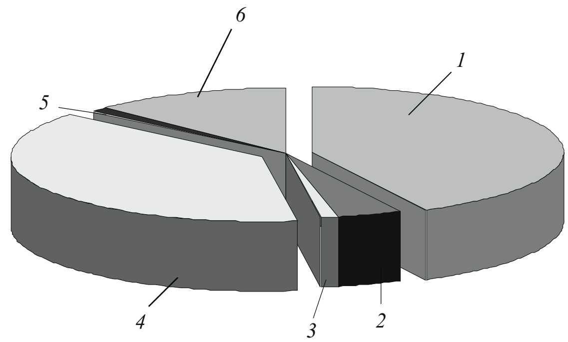


**Fig. 4.** Phase composition of foam zeolite sample with 13.8% alkali additive after firing at 850°C: *1*) amorphous phase, 38.60%; *2*) quartz, 9.97%; *3*) diopside, 3.75%; *4*) albite, 34.90%; *5*) hercynite, 1.01%, *6*) sanidine, 11.70%.

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